

# Influence of the microstructure on the magnetism of Co-doped ZnO thin films.

A. Fouchet, W. Prellier, and B. Mercey

*Laboratoire CRISMAT, UMR CNRS-ENSICAEN(ISMRA) 6508,  
6, Bld. du Maréchal Juin, F-14050 Caen, France*

(Dated: February 6, 2008)

## Abstract

The prediction of ferromagnetism at room temperature in Co-ZnO thin films has generated a large interest in the community due to the possible applications. However, the results are controversial, going from ferromagnetism to non-ferromagnetism, leading to a large debate about its origin (secondary phase, Co clusters or not). By carefully studying the micro-structure of various Co-ZnO films, we show that the  $\text{Co}^{2+}$  partly substitutes the ZnO wurtzite matrix without forming Co clusters. Surprisingly, the ferromagnetism nature of the films disappears as the Co content increases. In addition, our results suggest that the observed ferromagnetism is likely associated to a large amount of defects- close to the interface and strongly depending on the growth temperature- which may explained the spreading of the results.

PACS numbers:

## I. INTRODUCTION

Recently, Diluted Magnetic Semiconductors (DMS)<sup>1,2,3,4</sup> have become a very attractive subject due to the possibility of room temperature ferromagnetism in wide-band gap oxides.<sup>5</sup> Such materials might be integrated into semiconductors devices opening the route to spin-electronic technology at high temperature. First reports were dedicated to the cobalt-doped ZnO,<sup>6</sup> and TiO<sub>2</sub>,<sup>2,7</sup> and the manganese-doped ZnO.<sup>8</sup> Following these results, many materials showing ferromagnetism have been isolated so far.<sup>9,10,11,12</sup> Surprisingly, other reports did not evidence any ferromagnetism in the compounds<sup>13,14,15,16</sup> especially when made in bulk materials,<sup>17</sup> which has led to a hot debate about the origin of ferromagnetism in these materials. In particular, it is not clear whether ferromagnetism is originated from clusters,<sup>18,19,20</sup> secondary phases<sup>21</sup> or it is an intrinsic phenomenon.<sup>22,25</sup> Thus, it is important to answer the following questions:

- why are there so many non-reproducible reports?
- why is ferromagnetism relatively independent of the dopant and its concentration?<sup>25</sup>
- is the ferromagnetism intrinsic in Co-doped ZnO films?

During the last 5 years, several theoretical predictions raised the possibility of ferromagnetism with Curie temperature ( $T_C$ ) above room temperature in 3d-transition-metal-doped ZnO. Dietl *et al.*<sup>1</sup> suggested that wide band gap semiconductors are candidates for a high  $T_C$  and a large magnetization when 5% Mn is substituted into *p*-type [ $10^{20}\text{cm}^{-3}$ ]. Using *ab-initio* band structure calculation, Sato *et al.*<sup>23</sup> predicted a stabilization of the ferromagnetic state in 3d-transition metal doped ZnO. Recently, Coey *et al.*<sup>25</sup> proposed a model for high temperature ferromagnetism in dilute *n*-type magnetic semiconductor. This model is based on the formation of bound polaron magnetic mediated by shallow donor electrons.

>From these different theories and the experimental results, it appears that the role of defects is important.<sup>26</sup> Different scenarios are thusly possible. First, the presence of oxygen vacancies or interstitial zinc possibly result in an increase of the conductivity since they may create donor electrons.<sup>25</sup> Second, a large amount of cationic defect or excess of dopant can also lead to cluster or secondary phases. In addition, the defects might come from the growth techniques and the conditions used (temperature, oxygen pressure).<sup>4</sup> The spreading of the results by the different groups probably comes from the strong influence of the deposition parameters on the structure which is correlated to the magnetic properties.

In order to elucidate the origin of ferromagnetism and answer some of these questions, we have first undertaken a detailed microstructural analysis using transmission electron microscopy on the host matrix, ZnO, grown at various temperature. Second, we have correlated the magnetic properties and the microstructure of a series of cobalt-doped ZnO films. Third, we find the experimental tendency that the presence of defects in Co-ZnO films is necessary for the observation of room temperature ferromagnetism. Finally, we turn to an interpretation based on theoretical model.

## II. EXPERIMENTAL

The ZnO and Co-ZnO films were grown utilizing the pulsed laser deposition technique (Lambda Physik, KrF laser  $\lambda = 248 \text{ nm}$ )<sup>27</sup> by firing the laser alternatively on a zinc metal target (99.995 %) and on a cobalt metal target (99.995 %). These target were purchased (NEYCO, France) and were used without further preparation. All films are deposited on (0001)-oriented  $\text{Al}_2\text{O}_3$  substrates at a constant temperature under a flux of pure oxygen gas. Typical thickness of the films is about 300nm. The structural study was done by X-Ray diffraction (XRD) using a Seifert XRD 3000P for the  $\Theta - 2\Theta$  scans and the  $\omega$ -scan (tilting) with (Cu,  $\text{K}\alpha 1$  radiation  $\lambda = 0.15406 \text{ nm}$ ). The electron diffraction (ED) and electron microscopy observations were performed on JEOL 2011FEG electron microscope (tilt  $\pm 45^\circ$ ) equipped with Energy Dispersive Spectrometer (EDS) analyzer. This microscope is also fitted with a Scanning Transmission Electron Microscope equipment (STEM) to carry out high resolution scanning electron microscopy or EDS cartography. The resistivity measurements were measured in a Physical Properties Measurements System (PPMS) Quantum Design. Silver electrodes were deposited by thermal evaporation through a mask and contact between thin film and sample holder were realized with ultrasonic bonding (wire of Al-Si 99/1). The magnetization measurements were collected using a superconducting quantum interference device based magnetometer SQUID (Quantum Design MPMS-5).

### III. RESULTS

#### A. Temperature-dependance of the microstructure of ZnO films

Before understanding the magnetic properties of the cobalt-doped ZnO, a study of the influence of the deposition parameters on microstructure of the host matrix, ZnO, was performed. For this, the structural quality of a series of ZnO films grown under different growth conditions was investigated. One of the main deposition parameter is the substrate temperature (which is known to be of the most important parameter)<sup>28</sup> and the films were investigated using the XRD. Out-of-plane lattice parameter close 0.518 nm was obtained in the temperature range 500-700 °C, in agreement with the expected one.<sup>29</sup> In addition, the rocking curve recorded around the (0002) reflection measured for the films grown at 500, 600 and 700 °C are 0.4, 0.25 and 0.32°, respectively. Such values are commonly obtained for an oxide thin film and reflect, at least from these measurements, an average good crystallinity of the overall film (the instrument resolution is close to 0.2°). This means that, using a routine XRD analysis, there is no noticeable change and indicates that the subtle differences can only be seen with deeper analysis such as asymmetrical XRD or optical measurements.<sup>28</sup> To complete this analysis at such atomic scale, a microstructural analysis using transmission electron microscopy (TEM) was undertaken.

Figure 1 (a) and (b) show typical TEM images of two films grown at 600 and 700°C, respectively. The corresponding selected area diffraction are also presented. The images show a good crystallinity of the films. More precisely, the electron diffraction patterns (inset of Fig.1a, 1b) reveal two interesting features. First, the ED patterns reveal 6 spots as expected from a wurtzite structure (in agreement with the XRD)<sup>28</sup> and a film oriented with the *c*-axis perpendicular to the plane of the substrate. Second, the spots are well defined for the film at 700 °C but some broadening or parasite spots can be observed for the film grown at 600 °C. This suggests that the film is less crystallized when the temperature of the substrate is decreased, in agreement with our previous reports.<sup>28</sup> Note that the decrease of the crystalline quality with temperature is confirmed by the analysis of the films deposited at a temperature lower than 600 °C (not shown).

Furthermore, Fig.1c shows a plane view of the interfacial area between the film and the substrate of a film grown at 700 °C. In this picture a "moiré" contrast, resulting from the

superimposition of the two lattices, is observed. The Fourier transform from this part of the image (insert of Fig.1c) clearly shows that the two lattices are slightly misoriented (about  $1^\circ$ ). However this result raises the understanding of the misorientation of  $30^\circ$  between the film and the substrate already observed by the XRD.<sup>30</sup> In order to explain such a discrepancy, two features can be put forward. Firstly, this picture shows only the early stage of the growth, i.e. the first few cells grew on top of the substrate. The array of the oxygen atoms of the sapphire substrate, provides a good template to accommodate the first zinc ad-atoms despite the large difference between the lattice parameters of the two structures (lattice mismatch 16 %).<sup>31</sup> Secondly, when the thicker layers are grown, the lattice mismatch between the two structures plays the most important role and the cell of the film will rotate in order to accommodate this large mismatch. The thickness of this "accommodation layer" depends on the temperature of the growth. In others words, this "accommodation layer" is thin when the temperature is high whereas the "accommodation layer" is thick at a lower temperature. Such result is in agreement with Ashkenov *et al.* where a very thin nucleation layer (2-3 monolayers) with no cracks is observed on top of the  $\text{Al}_2\text{O}_3$  substrate for a ZnO film grown at high temperature ( $800^\circ\text{C}$ ).<sup>32</sup>

Since the crystallinity of the film grown at  $700^\circ\text{C}$  is higher than the one at  $600^\circ\text{C}$ , we have chosen to look only at a less crystallized film (i.e.  $600^\circ\text{C}$ ) and its evolution along the  $c$ -axis direction. Different areas of a film grown at  $600^\circ\text{C}$  were thusly observed. Figure 2 shows the electron diffraction patterns of this film, close to the surface (Fig.2 (a)) and close to the interface (Fig.2 (d)) and in between (Fig.2 (b) and (c)). When considering at the evolution of the ED patterns, it is clear that the 6 well defined peaks, close to the surface becomes a series of two rings, indicating a poor crystallization close to the interface. These diffraction images show that the film shows a gradient of crystallinity from the interface to the surface which is mostly due to the important lattice mismatch between the substrate and the film. However, we have noticed that such effect is enhanced when decreasing the temperature of the substrate. In other words, the less crystallized layer of the film close to the interface is increased when the temperature of deposition is decreased. It is also important to note that the polycrystalline layers close to the interface can not be observed with the standard XRD characterizations. Thus, it is necessary to perform microstructural measurements because it gives a local characterization whereas the XRD measurements give only an idea of the average crystallinity of the film. To explain the divergence of the  $30^\circ$

rotation observed by XRD measurements between the two lattices and the "moiré" with a tilting of  $1^\circ$  at the interface observed by HRTEM, the lattice mismatch must also be taken into account.

To summarize, the large strain induces the formation of a buffer layer at the interface, which can be polycrystalline. However, it can be reduced by an increasing of the deposition temperature (see above). This means that a stabilization of the structure with a rotation of the film parameters of  $30^\circ$  compared to the substrate is favoring by the increasing of the substrate temperature. Moreover, the use of high temperature increases the mobility of the ad-atoms and the size of the ZnO crystallites.<sup>28</sup> We believe that this is an explanation of the difference observed in the literature of Co-doped ZnO films as detailed hereafter. To confirm this, we have undertaken similar microstructural study of Co-doped ZnO film, following the same approach.

## **B. Temperature-dependance of the microstructure of Co-doped ZnO films**

### *1. The case of 1.66 % Co*

A low cobalt concentration (1.66 %) has been chosen in agreement with previous results because for such a composition, the presence of a secondary phase in the film is unlikely. The dependance of the magnetic properties on the growth conditions of a Co-ZnO film was analyzed. The films were grown at different deposition temperatures (500, 600 and 700  $^\circ\text{C}$ ) and the pressure of oxygen was varying from 0.05 to 0.15 *Torr*. As seen previously, the temperature tunes the crystallinity of the film. The oxygen pressure influences the resistivity with the creation of oxygen non-stoichiometry or interstitial zinc. Furthermore the study of the resistivity of the film could help us to understand the cause of the magnetic properties in the films.

By looking at the series of films, we find a tendency: the films are non-ferromagnetic when grown at 700  $^\circ\text{C}$  and are all ferromagnetic when deposited at 500  $^\circ\text{C}$  whatever the oxygen pressure is. This is evidenced in Figure 3, where the film synthesized at 500  $^\circ\text{C}$  displays an hysteresis loop in the ( $M-H$ ) curve with a saturation value of  $1.35 \text{ emu/cm}^3$  (corresponding to a saturation magnetization,  $M_S = 0.3 \mu_B/\text{Co}$ ) and a coercive field of  $\approx 100 \text{ Oe}$  (see inset of Fig. 3). A Curie temperature slightly above 300K is also observed on the  $M(T)$  curve,

confirming the ferromagnetic behavior.. Below 50  $K$ , a rapid increase of the magnetization is also observed. This paramagnetic contribution might be due to the low concentration of Co ions in the film which are not coupled to each other.<sup>33</sup> On the contrary, the film deposited at a higher temperature (700°C) does not show any hysteresis loop and its magnetization is close to zero. The situation is more complicated for the films grown at an intermediate temperature (for example at 600 °C). Indeed, these films can display a ferromagnetic (as seen in a previous report)<sup>30</sup> or a paramagnetic behavior. However, we have not be able to find a precise correlation between the observed magnetic behavior and the growth conditions of the films deposited at 600 °C. This indicates some lack of reproducibility which is more important at this temperature because 600 °C is an intermediate temperature between the two regions, and thus a very sensitive one.<sup>34,35</sup> To summarize, this study demonstrates first, the importance of temperature growth on the magnetic properties.<sup>36</sup> Second, the variation of oxygen pressure at a fixed temperature does not show any influence on the magnetic measurements: a magnetic transition is observed around 300  $K$  for all the films grown at 500 °C. Resistivity measurements show that the values at 300  $K$  are 0.86  $\Omega.cm$  and 387  $\Omega.cm$ . for the film grown at 0.05 Torr and 0.15 Torr, respectively. The rocking curve is constant to a value around 0.43°, close to the instrumental limit of 0.15° and the one of the Al<sub>2</sub>O<sub>3</sub> substrate of 0.2°. This indicates that the oxygen pressure does not have a strong influence on the average crystallinity of the film. The inhomogeneity in the transport measurements compared to the constant value Curie temperature confirms the independence of the number of carriers on the magnetic properties, in contradiction with previous reports.<sup>1,9</sup> The presence of ferromagnetic or ferrimagnetic Co-based phases can also be excluded *a priori*, due to the low concentration of cobalt since it is difficult to believe that a small amount of Co will lead to a magnetic phase that is not observed neither in XRD measurements nor in HRTEM analysis. Furthermore, the shape of the  $M(T)$  curve does not exhibit superparamagnetic behavior with a blocking temperature, but a well defined Curie transition which means that there is not individual domains of elements that have ferromagnetic properties.<sup>24</sup> Anyway, these results indicate a correlation between the crystallinity of the film and their magnetic properties. Surprisingly, an ill crystallize films (rocking curve around 0.4-0.5°) always leads to a ferromagnetic transition whereas a highly crystallized one (rocking curve around 0.26-0.3° for the films grown at 700 °C) is rarely ferromagnetic. Thus, we think that a large number of defects is necessary to observe the ferromagnetic properties which will be discuss

later.<sup>37</sup>

## 2. Variation with Co content

Similar kind of study was done keeping the oxygen pressure to 0.1 Torr (since it is not influencing the magnetic characteristics) but varying the Co concentration from 5 to 10 %, and changing the deposition temperature between 500 and 700 °C. The results show that only the film grown at 500 °C with 5 % of Co doping exhibit a (weak) magnetic signal with a magnetization of 0.1  $emu/cm^3$  (under a magnetic field of 100 Oe) , while the film at 10 % cobalt is paramagnetic.

In addition, transport measurements revealed that all films are highly resistive with a value at 300 K of 350  $\Omega.cm$  for the film at 5 % and, more than 450  $\Omega.cm$  for the film with 10 % of Co. This confirms the previous study<sup>6</sup> where the crystallinity was decreasing with the concentration of cobalt in the film and leads to the creation of acceptors, increasing the resistivity of the film.

In order to confirm the relations between magnetism and defects, two films at high (10 %) and low Co-doping (1.66 %) were analyzed by TEM (Figure 4). Fig.4 (a) shows a cross section TEM of a film having 10 % of Co. At the interface, a difference of crystallinity between the substrate and the film is seen. Furthermore, the diffraction pattern of this part shows a well aligned diffraction peaks assimilate to the substrate with a c-axis perpendicular to the interface. The film presents different rings, clearly showing the polycrystalline nature of the structure close to the interface. Different ED analysis performed on several areas of the film showed that the crystallinity is increased when approaching the surface. Fig. 4 (b) shows similar images for a 1.6 % Co-doped films. Despite a good crystal quality showed also by ED, some defects can be observed. In the insert of figure 4 (b) is zoomed a tilt of the structure of 60°. This analysis at the atomic scale (few nm) must show the presence of any clusters having a size of minimum 6 nm to be seen by HRTEM.<sup>38</sup> This investigation was carried out on a high number of different crystals for both films, but no clusters have been detected and cobalt seems to have a good dilution in the matrix. An analysis with STEM also confirms the good distribution of the cobalt in ZnO.



#### IV. DISCUSSION

Close to the substrate interface, the crystallinity of the film influenced by the growth temperature and the Co content, is not satisfactory or at least, not as good as in the upper layers: a low substrate temperature leads to a high disorder of the Co-doped ZnO film. This is due to the large lattice mismatch between the film and the substrate. The effect of the temperature can be well understood by the increase of kinetic energy of the particles at the surface of the film, which improves the crystallinity and, consequently decreases the number of defects.<sup>39</sup> For this reason, Saeki *et al.* have used a ZnO buffer layer to improve the quality of the Co-ZnO films. However, in that case a post-annealing was necessary to obtain a ferromagnetism behavior in the film since in the as-grown the Co-ZnO is antiferromagnetic.<sup>34</sup>

In the present study, it has been showed that in order to get a ferromagnetic film at 300 K, a low Co concentration *and* a low growth temperature are required. If the Co concentration is larger than 5 %, then the magnetization becomes negligible. Thus, despite the disorder increasing in the structure with the amount of cobalt,<sup>30</sup> the magnetization shows a paramagnetic behavior.

Furthermore, the formation of any clusters or second phases was *a priori* minimized because of the particular deposition technique which is alternative deposition. This process indeed favors the dispersion of the cobalt inside the structure. For this, two metallic targets are held on a carousel. The laser, using the rotation of the two targets, fired on the zinc followed by the cobalt target. For example, to obtain 5 % cobalt doped film, it is necessary to fire 19 pulses on Zn target and then 1 pulse on the Co target. The deposition rate is close to 0.052 nm/pulse. Thus, one cobalt pulse is sandwiched between 2 ZnO layers made up 19 pulses each. It is unlikely that the quantity of cobalt between two layers of ZnO is sufficient to create some cobalt clusters. Furthermore, a gradient of diffusion (due to the temperature of the substrate) will appear, favoring the migration and the dilution of cobalt in the ZnO structure. A low growth temperature unlikely decreases the Co diffusion, and might induce the presence of Co-rich phases (i.e. Co clusters or secondary phases). These phases can lead to ferromagnetism or ferrimagnetism behaviors. Such result might explain the similarity between the films grown at 500°C under various oxygen pressure. However, based on the XRD and the HRTEM no Co-rich phases have been evidenced and, this model can not explain the antiferromagnetic behavior at high Co concentration.

Another possible explanation for the observation of ferromagnetic is as follow, depending on the crystallinity and the Co concentration. At low doping, the short interactions mechanisms like superexchange and Zener double-exchange interaction can be avoided, because of the low probability to have two cobalt neighbor atoms. At longer range ferromagnetic exchange, the *RKKY* model can be also avoided due to the *n*-type behavior of ZnO and the low number of carriers in the films. Thus, these models can not be used to explain the ferromagnetism. We believe that the recent model of the bound magnetic polaron used in the *n*-type semiconductors by shallow donors is more appropriate.<sup>25</sup> In this model, Coey *et al.* utilized the general formula for the oxide:  $(A_{1-x}Co_x)(O\Box_{\partial})$  where *A* is nonmagnetic cation and  $\partial$  is the donor defect.<sup>25</sup>

Experimentally, this means that the ferromagnetism appears only with a high probability of donor defects in the film, at low deposition temperature compared to 700 °C where the crystal defects are less present. Finally, the high defect concentration close to the interface leads to the formation of an impurity band, which is polarized by exchange with magnetic elements. This is confirmed by the value of the saturation magnetization which is equal to  $(0.3 \pm 0.1) \mu_B/Co$ . Surprisingly, this value is smaller compared to the  $Co^{2+}$  spin state in a tetrahedral crystal field (low spin=  $1 \mu_B$  or high spin=  $3 \mu_B$ ). However, if we only consider the cobalt atoms having an environment of defects that are at the origin of ferromagnetism (i.e. for example, 1/3 of the film), the value would be in the order of  $1 \mu_B/Co$ . This reinforced the fact that the ferromagnetism originated from the "bulk" material and this is likely the origin of ferromagnetism at low doping concentration.<sup>40</sup> It should also be pointed out that in these experiments, the oxygen pressure induces large changes in resistivity (see above). As consequence and, based on this model, the oxygen pressure should have an effect on the magnetization. Since it is not the case, this means that a detailed study on the nature of the defects is required (structural defects, oxygen and zinc vacancies, interstitials etc.).<sup>41</sup>

At high doping, the situation is more simple. Due to the antiferromagnetic coupling between the Co atoms, which comes from the short magnetic interactions (resulting from the high probability to have two cobalt neighbors), the sample exhibits paramagnetism.

## V. CONCLUSION

The comparison of microstructural and macrostructural analysis of a series of Co-doped ZnO films clarified the conditions to obtain interesting magnetic properties. Only the films at low cobalt doping *and* grown at low temperature display ferromagnetism at room temperature. Whereas the number of carrier in the film does not seem to control the magnetism, the defects are necessary to observe ferromagnetic properties. In spite of the high concentration of cobalt in the structure, the microstructural analysis do not show cobalt clusters, revealing an homogeneous cobalt distribution in the ZnO matrix. This is confirmed by the magnetic measurement which do not exhibiting superparamagnetism behavior. Based on these experiments, we believe that the ferromagnetism is intrinsic and result from long-range interactions induced by the defects. The determination of synthesis condition favoring the reproducibility of magnetic properties might be the beginning point from the elaboration of some devices for the spin polarization.

Partial financial support from the Center Franco-Indien pour la promotion de la recherche Avancée/Indo-French Center for the promotion of advanced Research (CEFIPRA/IFCPAR) under Project No. 2808-1 is acknowledged. The Centre National de la Recherche Scientifique (CNRS) and the "Conseil Régional de Basse Normandie" is also supporting this work through a BDI fellowship.

- 
- <sup>1</sup> T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* 287 (2000) 1019.
- <sup>2</sup> Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, *Science* 291 (2001) 894.
- <sup>3</sup> W. Prellier, A. Fouchet and B. Mercey, *J. Phys.: Cond. Mat.* 15 (2003) R1583.
- <sup>4</sup> R. Janisch, P. Gopal and N.A. Spaldin, *J. Phys.: Cond. Mat.* 17 (2005) R657.
- <sup>5</sup> S.J. Pearton, C.R. Abernathy, M.E. Overberg, G.T. Thaler, and D.P. Norton, N. Theodoropoulou and A.F. Hebard, Y. D. Park, F. Ren and J. Kim, L. A. Boatner, *J. Appl. Phys.* 93 (2003) 1.
- <sup>6</sup> W. Prellier, A. Fouchet, B. Mercey, Ch. Simon and B. Raveau, *Appl. Phys. Lett.* 82 (2003) 3490.
- <sup>7</sup> S.R. Shinde, S.B. Ogale, S. Das Sarma, J.R. Simpson, H.D. Drew, S.E. Lofland, C. Lanci, J.P. Buban, N.D. Browning, V.N. Kulkarni, J. Higgins, R.P. Sharma, R.L. Greene, T. Venkatesan, *Phys. Rev. B* 67 (2003) 115211.
- <sup>8</sup> P. Sharma, A. Gupta, K. V. Rao, F. J. Owens, R. Sharma, R. Ahuja, J. M. Osorio Guillen, B. Johansson and G. A. Gehring, *Nature Mater.* 2 (2003) 673.
- <sup>9</sup> S.N. Kale, S.B. Ogale, S.R. Shinde, M. Sahasrabuddhe, V.N. Kulkarni, R.L. Greene, T. Venkatesan, *Appl. Phys. Lett.* 82 (2003) 2100.
- <sup>10</sup> K. Rode, A. Anane, R. Mattana, and J.-P. Contour, O. Durand and R. Lebourgeois, *J. Appl. Phys.* 93 (2003) 7676.
- <sup>11</sup> Z. Yin, N. Chen, C. Chai and F. Yang, *J. Appl. Phys.* 96 (2004) 5093.
- <sup>12</sup> A. S. Risbud, N. A. Spaldin, Z. Q. Chen, S. Stemmer and R. Seshadri, *Phys. Rev. B* 68 (2003) 205202.
- <sup>13</sup> Z. Jin, T. Fukumura and M. Kawasaki, K. Ando and H. Saito, T. Sekiguch, Y. Z. Yoo, M. Murakami, Y. Matsumoto, T. Hasegawa and H. Koinuma, *Appl. Phys. Lett.* 78 (2001) 3824.
- <sup>14</sup> S. Kolesnik and B. Dabrowski, *J. Appl. Phys.* 96 (2004) 5379.
- <sup>15</sup> G. Lawes, S. Risbud, P. Ramirez, Ram Seshadri, *Phys. Rev. B* 71 (2005) 045201.
- <sup>16</sup> R. C. Budhani, P. Pant, R.K. Rakshit, K. Senapati, S. Mandal, N.K. Pandey and J. Kumar, *J. Phys. Cond. Matter* 17 (2005) 75.
- <sup>17</sup> S. W. Yoon, S.-B. Cho, S. C. We, S. Yoon, and B. J. Suh, H. K. Song and Y. J. Shin, *J. Appl. Phys.* 93 (2003) 7879.

- <sup>18</sup> J.H. Park, M.G. Kim, H.M. Jang and S. Ryu, Appl. Phys. Lett. 84 (2004) 1338.
- <sup>19</sup> D.H. Kim, J.S. Yang, KW. Lee, S. D. Bu and T. W. Noh, S.-J. Oh, Y.-W. Kim, J.-S. Chung, H. Tanaka, H.Y. Lee, and T. Kawai, Appl. Phys. Lett. 81 (2002) 2421.
- <sup>20</sup> D.P. Norton, M.E. Overberg, S.J. Pearton, and K. Pruessner, J.D. Budai, L.A. Boatner and M.F. Chisholm, J.S. Lee, Z.G. Khim, and Y.D. Park, R.G. Wilson, Appl. Phys. Lett. 83 (2003) 5488.
- <sup>21</sup> D.C. Kundaliya, S.B. Ogale, S.E. Lofland, S. Dhar, C. J. Metting, S. R. Shinde, Z. Ma, B. Varughese, K. V. Ramanujachary, L. Salamanca-Riba and T. Venkatesan, Nature Mater. 3 (2004) 709.
- <sup>22</sup> N.H. Hong, J. Sakai and W. Prellier, Phys. Rev. B 70 (2004) 195204.
- <sup>23</sup> K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 39 (2000) L555.
- <sup>24</sup> J.H. Park, M.G. Kim, H.M. Jang, S. Ryu and Y.M. Kim, Appl. Phys. Lett. 84 (2004) 1338.
- <sup>25</sup> J.M.D. Coey, M. Venkatesan and C.B. Fitzgerald, Nature Materials 4 (2005) 173.
- <sup>26</sup> G. Bouzerar, T. Ziman and J. Kudrnovský, Phys. Rev. B 72 (2005) 125207.
- <sup>27</sup> E. Rauwel Buzin, W. Prellier, Ch. Simon, S. Mercone, B. Mercey, B. Raveau, J. Sebek and J. Hejtmanek, Appl. Phys. Lett. 79 (2001) 674.
- <sup>28</sup> A. Fouchet, W. Prellier, B. Mercey, L. Méchin, V.N. Kulkarni, T. Venkatesan, J. Appl. Phys. 96 (2004) 3228.
- <sup>29</sup> JCPDS-International Center for diffraction Data, Card No. 05-0664 (2001), R.R. Reeber, J. Appl. Phys. 41 (1970) 5063.
- <sup>30</sup> A. Fouchet, W. Prellier, P. Padhan, Ch. Simon and B. Mercey, V.N. Kulkarni and T. Venkatesan, J. Appl. Phys. 95 (2004) 7187.
- <sup>31</sup> R.D. Vispute, V. Talyansky, Z. Trajanovic, S. Choopun, M. Downes, R.P. Sharma and T. Venkatesan, M.C. Woods, R.T. Lareau and K.A. Jones, A.A. Iliadis, Appl. Phys. Lett. 70 (1997) 2735.
- <sup>32</sup> N. Ashkenov, B.N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E. M. Kaidashchev, A. Kasic, M. Schubert and M. Grundmann, G. Wagner, H. Neumann, V. Darakchieva, H. Arwin, and B. Monemar, J. Appl. Phys. 93 (2003) 126.
- <sup>33</sup> H.-J. Lee, S.-Y. Jeong, C.R. Cho and C.H. Park, Appl. Phys. Lett. 81 (2002) 4020, J.H. Kim, W.K. Choo, H. Kim, D. Kim and Y. Ihm, J. Korean Phys. Soc. 42 (2003) S258.

- <sup>34</sup> H. Saeki, H. Matsui, T. Kawai and H. Tabata, J. Phys. Cond. Matter 16 (2004) S5533.
- <sup>35</sup> K. Ueda, H. Tabata and T. Kawai, Appl. Phys. Lett. 79 (2001) 988.
- <sup>36</sup> A.K. Pradhan, K. Zhang, S. Mohanty, J.B. Dadson, D. Hunter, J. Zhang, D.J. Sellmyer, U.N. Roy, Y. Cui, A. Burger, S. Mathews, B. Joseph, B.R. Sekhar and B.K. Roul, Appl. Phys. Lett. 86 (2005) 152511.
- <sup>37</sup> N.H. Hong, J. Sakai and N.T. Huong, N. Poirot, A. Ruyter, Phys. Rev. B 72 (2005) 45336.
- <sup>38</sup> S.R. Shinde, S.B. Ogale, J.S. Higgins, H. Zheng, A.J. Millis, V.N. Kulkarni, R. Ramesh, R.L. Greene and T. Venkatesan, Phys. Rev. Lett. 92 (2004) 166601.
- <sup>39</sup> Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. 98 (2005) 041301.
- <sup>40</sup> In that case, "bulk" is associated to intrinsic phenomena. It means the overall "bulk" film by opposition to the clusters or secondary phase present in a film.
- <sup>41</sup> A.F. Kohan, G. Ceder, and D. Morgan, Chris G. Van de Walle, Phys. Rev. B 61 (2000) 15019.

Figures Captions:

Figure 1: High resolution transmission electron microscopic image of ZnO film and Fourier transformation pattern (inset). All crystal fragments are oriented with  $c$ -axis parallel to the electron beam. (a) Film grown at 600 °C with on the Fourier transformation, 6 peaks characteristic of the 6-fold symmetry of ZnO. The pattern (b) and (c) are film grown at T=700 °C. The first one shows HRTEM of crystal in film and the last one shows the interface with "moiré" phenomena.

Figure 2: Different diffraction pattern taken from the interface of the film until close to the surface. An evolution of the crystallinity is observed with 6 well defined peaks close to the surface and a broadening of these diffraction peaks along the  $c$ -axis until the interface.

Figure 3: (M-T) curve of zero field cooled and field cooled (100 Oe) for a Co:ZnO: 1.66 % thin film grown at 500 °C. The inset presents the (M-H) curves at 10K of films grown at 500 and 700 °C. The coercive field of the film grown at 500 °C is about 100 Oe. All these curves have corrected from the substrate component.

Figure 4: HRTEM images of Co-ZnO films deposited at 600 °C. (a) is a cross section of a high doping Co-ZnO: 10 %. The well crystallized right part is the substrate and at left the film. The inset is the diffraction pattern of the interface. The aligned peaks are the substrate and the rings are due to the film. (b) is the film doped with 1.6 % cobalt with  $a$  and  $b$  axis in-plane.

This figure "Figures\_Page\_1.jpg" is available in "jpg" format from:

<http://arXiv.org/ps/cond-mat/0604468v1>



This figure "Figures\_Page\_2.jpg" is available in "jpg" format from:

<http://arXiv.org/ps/cond-mat/0604468v1>

This figure "Figures\_Page\_3.jpg" is available in "jpg" format from:

<http://arXiv.org/ps/cond-mat/0604468v1>

This figure "Figures\_Page\_4.jpg" is available in "jpg" format from:

<http://arXiv.org/ps/cond-mat/0604468v1>